

Title: "Coating for drinking water pipelines"

THIS INVENTION RELATES to two-part, rapid setting coating systems useful as internal linings for pipelines carrying drinking water.

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The use of two-part coating systems, in particular those based on liquid epoxide resins and polyamine curing agents, to form protective linings for drinking water pipelines is well known. Such two-part systems have a demonstrable track record for both the "in-situ" refurbishment of existing water mains and for the protection of new pipelines. They provide thin, smooth linings with excellent carrying capacity and long term durability. However, these systems exhibit one main limitation for "in-situ" use in that due to their relatively slow hardening characteristics it is necessary to allow the coatings to harden minimally for 16 hours before returning the pipeline to service.

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European Patent Application EP-A-0936235 discloses the use of aliphatic polyisocyanates blended with liquid epoxide resin or non-reactive resin, in combination with selected aromatic diamines, to provide rapid setting coating compositions useful as internal linings for pipelines, in particular as "in-situ" applied linings for refurbishment of drinking water pipelines. Such compositions, by virtue of their rapid setting characteristics, allow return to service in 2 hours or less with no adverse effects on water quality.

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EP-A-0936235 teaches the use of a liquid epoxide resin or non-reactive resin in order to extend the gel time, reduce the heat of reaction and reduce the shrinkage of the pure polyurea systems obtained from the combination of aliphatic polyisocyanate(s) with aromatic polyamine(s).

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The present invention provides a two-part coating system that can be applied to internal pipeline surfaces so as to form, at a high cure rate, an impervious lining suitable for contact with drinking water. By virtue of its rapid setting characteristics and insensitivity to moisture, the system of the present invention is particularly useful as an "in-situ" applied lining for refurbishment of existing drinking water pipelines.

The first part of a two-part coating system according to the present invention comprises one or more aliphatic polyisocyanates, optionally blended with one or more "amine reactive" resins and/or non-reactive resins.

5 The aliphatic polyisocyanate(s) employed in the invention can be any organic isocyanate compound containing at least two isocyanate functional groups, said isocyanate groups being aliphatic in nature. Suitable polyisocyanates include hexamethylene-1,6-diisocyanate; 2,2,4-trimethylhexamethylene diisocyanate; isophorone diisocyanate; 4,4'-dicyclohexylmethane diisocyanate. Alternatively, reaction products or prepolymers derived from the above may be
10 utilised. For the purposes of the present invention, the preferred polyisocyanates are derivatives of hexamethylene-1,6-diisocyanate. The polyisocyanate compounds have a preferred isocyanate content of between 5 and 50%, with 20-25% being particularly preferred.

15 The "amine reactive" resin(s) can be any compound containing functional groups which are capable of reacting with primary or secondary amines. Useful materials include epoxy functional compounds and any compounds containing unsaturated carbon-carbon bonds capable of undergoing "Michael Addition" with polyamines, e.g. monomeric or oligomeric polyacrylates. For the purposes of the present invention, liquid epoxide resins or oligomeric polyacrylates are preferred.

20 Non-reactive resins, whilst not currently preferred in the present invention, may be employed provided that they have no resulting adverse effects on water quality.

25 The second part of a two-part system according to the present invention comprises one or more polyamines.

Preferably, the second part of the system comprises one or more aromatic polyamines, optionally blended with one or more oligomeric polyamines.

30 The aromatic polyamine employed can be any organic compound containing at least two primary or secondary amine groups, wherein said amine groups are substituted directly to an aromatic

moiety. Suitable aromatic polyamines include diethyl toluenediamine; dimethylthio toluenediamine; 4,4'-methylenebis (2-isopropyl-6-methylaniline); 4,4¹-methylenebis (2,6-diisopropylaniline); 4,4¹-methylenbis (2,6-dimethylaniline); 4,4¹-methylenbis (2,6-diethylaniline); 4,4¹-methylenebis (2-ethyl-6-methylaniline); 4,4¹-methylenebis (3-chloro-2,6-diethylaniline). For the purposes of the present invention, diethyl toluenediamine is particularly preferred.

The oligomeric polyamine can be any higher molecular weight organic compound containing at least two primary or secondary amine groups, said amine groups being either aliphatic, cycloaliphatic or aromatic in nature. Suitable compounds include poly (oxypropylene) diamines, poly (oxypropylene) triamines, poly (oxytetramethylene)-di-p-aminobenzoates. For the purposes of the present invention, the preferred compounds are poly (oxypropylene) diamines and poly (oxytetramethylene) di-p-aminobenzoates. The preferred oligomeric polyamines have a molecular weight in the range 400-6000, with molecular weights of 500-3000 particularly preferred. Whilst not currently preferred in the present invention, a second part composed solely of oligomeric polyamines or non-aromatic polyamines may be employed provided that there are no resulting adverse effects on water quality.

Various two-part systems embodying the invention are described below, by way of non-limiting example.

EXAMPLES

Table 1 below shows the results obtained when the liquid epoxide resin (Diglycidyl ether of Bisphenol A, "BADGE") in the preferred formulation(s) set out in European Patent Application EP-A-0936235 was replaced by alternative amine reactive resins, viz. monomeric or oligomeric polyacrylates.

TABLE 1

Amine Reactive Resin	Addition Level (Parts per 100 of polyiso-cyanate)	Film Set Time (Mins) 1 mm Film @ 3°C	Linear Shrinkage (%)	Film Integrity in Presence of Water
BADGE	0	2.5	0.150	Excellent
	20	4	0.090	Excellent
	40	5	0.040	Excellent
Trimethylol-propane triacrylate	0	2.5	0.150	Excellent
	20	3.5	0.100	Excellent
	40	4.5	0.050	Excellent
Penta-erythritol triacrylate	0	2.5	0.100	Excellent
	20	4	0.085	Excellent
	40	5	0.035	Excellent
Dipenta-erythritol pentaacrylate	0	2.5	0.150	Excellent
	20	4	0.090	Excellent
	40	5	0.040	Excellent

It can be seen from these results that other, "amine reactive" resins e.g. monomeric or oligomeric polyacrylates can usefully reduce the shrinkage of aliphatic polyisocyanate - aromatic polyamine systems, whilst still retaining rapid setting capability at low temperatures under adverse (wet) conditions.

Table 2 below shows the results obtained when the basic aliphatic polyisocyanate-aromatic polyamine system was modified by blending oligomeric polyamines with the aromatic polyamine.

TABLE 2

Aromatic polyamine/ oligomeric polyamine ratio w/w	Oligomeric polyamine	Film Set Time (Mins) 1 mm Film @ 3°C	Linear Shrinkage (%)	Film Integrity in Presence of Water
	Poly(oxy-propylene) diamine	3.5 Mins	0.030	Excellent

Aromatic polyamine/ oligomeric polyamine ratio w/w	Oligomeric polyamine	Film Set Time (Mins) 1 mm Film @ 3°C	Linear Shrinkage (%)	Film Integrity in Presence of Water
50/50	Poly(oxytetra-methylene)-Di-p-amino-benzoate	4.5 Mins	0.027	Excellent
	50/50 Blend (w/w) of the above	4 Mins	0.028	Excellent
	Poly(oxy-propylene) diamine	4 Mins	0.028	Excellent
40/60	Poly(oxytetra-methylene)-Di-p-amino-benzoate	5 Mins	0.025	Excellent
	50/50 Blend (w/w) of the above	4.5 Mins	0.026	Excellent
	Poly(oxy-propylene) diamine	Gelled instantly	N/A	N/A
0/100	Poly(oxytetra-methylene)-Di-p-amino benzoate	8 Hours	0.005	Excellent
	50/50 Blend (w/w) of the above	5 Mins	0.016	Excellent

It can be seen from comparison of these results against those illustrated in Table 1 that the incorporation of oligomeric diamines usefully reduces the shrinkage of the basic aliphatic polyisocyanate-aromatic polyamine system, whilst again retaining the rapid film set and insensitivity towards moisture.

Table 3 below shows the results obtained from combining the work illustrated in Tables 1 and 2. In the examples shown, the oligomeric polyamine was a 50/50 (w/w) blend of poly(oxypropylene) diamine and poly(oxytetramethylene)di-p-aminobenzoate.

TABLE 3

Aromatic Polyamine/ Oligomeric Polyamine Ratio w/w	Amine Reactive Resin	Addition level (Parts per 100 of polyiso-cyanate)	Film Set Time (Mins) 1 mm Film c@ 3°C	Linear Shrinkage (%)
	BADGE	20	4.5	0.025
		40	5	0.023
50/50	Dipenta- erythritol pentaacrylate	20	4.5	0.024
		40	5	0.022
	BADGE	20	5	0.023
		40	5.5	0.022
40/60	Dipenta- erythritol pentaacrylate	20	5	0.022
		40	5.5	0.020

In all cases, the film integrity under wet conditions was excellent.

It can be seen from these results that inclusion of the "amine reactive" resin can yield further reductions in shrinkage without significantly impacting on the film set time at low temperature.

Table 4 below shows the results obtained when a number of compositions representative of some of the preferred forms of the invention were evaluated for suitability for contact with drinking water in accordance with the requirement of BS 6920:2000. In all cases the coating compositions were applied at a nominal film thickness of 1 mm and allowed to cure for 30 minutes at 3°C prior to commencement of testing. In examples illustrated, the oligomeric polyamine "blend" was a 50/50 (w/w) blend of poly(oxypropylene) diamine and poly(oxytetramethylene)-di-p-aminobenzoate, with the "amine reactive" resin employed at an addition level of 25 parts per 100 of polyisocyanate (w/w).

TABLE 4

System	Oligomeric Polyamine	Aromatic Polyamine/ Oligomeric Polyamine Ratio w/w	Amine Reactive Resin	BS6920:2000 Test Result
A		100/0	Dipenta-erythritol pentaacrylate	PASS
B	Poly(oxypropylene) diamine	50/50		PASS
C	Poly(oxytetramethylene)-Di-p-amino-benzoate	50/50		PASS
D	Blend	50/50		PASS
E	Blend	50/50	BADGE	PASS
F	Blend	50/50	Dipenta-erythritol pentaacrylate	PASS

These results show that the invention allows quite wide formulatory latitude in designing coating systems which will set rapidly under adverse conditions (for example when applied underground, in-situ to an existing drinking water pipeline) without having any deleterious effects on water quality.

Table 5 below illustrates some of the differences in physical and mechanical properties of the compositions detailed in Table 4. All the compositions were cured for 24 hours prior to testing. Flexural properties were determined in accordance with BS EN ISO 178:1997 and tensile properties in accordance with BS EN ISO 527:1996.

TABLE 5

System	Flexural Strength (M Pa)	Tensile Strength (M Pa)	Elongation @ Break (%)
A	55.2	28.4	2
B	43.0	29.5	40
C	52.0	33.0	10
D	44.8	28.0	30
E	43.5	27.2	35
F	44.0	27.7	35

These results illustrate that variations in composition, within the scope of the invention, allow the design of coating systems to meet specific design criteria whilst still satisfying the key requirements for in-situ application to drinking water pipelines.

In the present specification “comprises” means “includes or consists of” and “comprising” means “including or consisting of”.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.